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A homologous series of crown-ether-complexed alkali metal amides as discrete ion-pair species: synthesis and structures of $[M(12\text{-crown-}4)_2][PyNPh \cdot PyN(H)Ph]$ ($M = Li$, Na and K)

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Abstract

Reaction between one equivalent of *n*-butyllithium and 2-phenylaminopyridine, in the presence of 12-crown-4 ether (12C4) in toluene, affords the discrete ion-pair complex $[\{Li(12C4)_2\}\{N(Py)(Ph) \cdot HN(Py)(Ph)\}]$ (**1**), in which the secondary amine proton is hydrogen-bonded to the secondary amide anion. Compound **1** is the sole isolable product of this reaction, irrespective of the amount of lithium alkyl employed, metallation never exceeding 50%. Metathesis of **1** with sodium- or potassium-*tert*-butoxide affords the homologous complexes $[\{Na(12C4)_2\}\{N(Py)(Ph) \cdot HN(Py)(Ph)\}]$ (**2**) and $[\{K(12C4)_2\}\{N(Py)(Ph) \cdot HN(Py)(Ph)\}]$ (**3**), respectively. Compounds **1**, **2** and **3** have all been characterised by X-ray crystallography, NMR spectroscopy and elemental analysis.

Keywords: Lithium; Sodium; Potassium; Amide ligands; 12-Crown-4; Crystal structures

1. Introduction

The structure and reactivity of alkali metal derivatives of alkyls, amides, imides and alkoxides has been the subject of intense interest over the past twenty years [1–6]. As a consequence of the highly ionic bonding in these systems, the structures adopted in solution and in the solid state are highly dependent upon the metal, the steric and electronic properties of the anionic ligand, and the presence or absence of Lewis base co-ligands. As a general rule, the introduction of multidentate ligands reduces the extent of aggregation of such complexes and renders them more reactive. With this in mind, we recently became interested in combining multidentate crown ether ligands with alkali metal amides in a systematic investigation of the structural changes manifested by a change in metal or in denticity of the crown. As part of an ongoing study, we have previously reported [7–9] structural investigations of alkali metal complexes of the secondary amine 2-trimethylsilylaminopyridine with 12-crown-4 (12C4) and 15-crown-5 (15C5), which revealed a range of structural motifs including monomer, dimer, discrete 'ate' ion pairs, and heterobimetallic ion triplets. In these studies, only the alkali metal or crown was modified. We report here our preliminary studies of the 12C4 complexes of alkali metal derivatives of the closely related secondary amine 2-phenylaminopyridine, to assess the structural impact of substituting the trimethylsilyl group with a phenyl ring, as these substituents possess different electronic and steric properties. A number of homometallic alkali metal complexes of 2-phenylaminopyridine have been reported previously [10–16] and, in general, aminopyridine complexes have found widespread applications as supporting ligands for main group (s and p block), lanthanide and transition metals [17].

2. Results and discussion

Contrary to our initial expectations, treatment of the secondary amine 2-phenylaminopyridine, in the

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presence of 12C4 in toluene, with one equivalent of *n*-butyllithium did not afford the desired complex [{LiN(Py)(Ph)}(12C4)]. Instead, the sole isolable product (Eq. (1)) was consistently the complex $[\{\mathrm{Li}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)}\cdot\mathrm{HN(Py)(Ph)}\}]$ (**1**). The ^{1}H and ^{13}C NMR spectra are in accord with the structure formulated, and the incomplete metallation is revealed by the sharp signal at 8.22 ppm in the ^{1}H NMR spectrum, characteristic of an amine proton. Satisfactory microanalysis was obtained for **1**.

$$2\mathrm{Bu}^n\mathrm{Li} + 2\mathrm{PyN(H)Ph} + 2(12\mathrm{C}4) \rightarrow [\{\mathrm{Li}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)} \cdot \mathrm{HN(Py)(Ph)}\}] + \mathrm{Bu}^n\mathrm{Li} \qquad (1)$$

The incomplete metallation of 2-phenylaminopyridine was unexpected and naturally called into question the molarity of the *n*-butyllithium solution. However, the same stock solution was used in the preparation of related compounds with high, sometimes quantitative, yields [7–9]. Subsequent titration revealed the *n*-butyllithium solution to be approximately 2.5 M, as expected. With low molarity of solution as an explanation for the incomplete metallation apparently ruled out, we sought another reason. We note that the complex $[\{\mathrm{Li[N(Py)(Ph)]HN(Py)(Ph)}\}_2]$, previously reported by Polamo and Leskelä [14], was consistently isolated, despite refluxing in toluene for one week. It therefore seemed likely to us that the problem was steric, or Lewis base mediated, in origin. Indeed, the solvent dependency of deprotonation of silyl-substituted alkyl and amide pyridines has been demonstrated previously [18,19]. The Polamo and Leskelä complex appears to be out of line with the lithium, sodium, and potassium complexes of 2-phenylaminopyridine reported by Clegg and co-workers [10–14]. However, in each of these cases a strong Lewis base donor was present in the synthesis, which may have facilitated full metallation. This seems credible, given that, with the same batch of *n*-butyllithium, no problems were encountered in synthesising the previously reported complex $[\{\mathrm{Li(PyNPh)(HMPA)}\}_2]$ (HMPA = hexamethylphosphoramide) in high (ca 90%) yield [11], and that we have previously observed dramatically different outcomes to reactions depending upon which crown ether is employed [7,8]. Inspection of the crystal structure of $[\{\mathrm{Li[N(Py)(Ph)]HN(Py)(Ph)}\}_2]$ [14] reveals that the NH functionalities are locked away in the core of the molecule, sterically protected by the phenyl rings; the implication is that a metal larger than lithium, and/or a suitable Lewis base, is required to open up the dimer and expose the NH functionalities to further deprotonation. This assertion is supported by the following observations: (i) using the same stock solution of *n*-butyllithium, full lithiation occurs in the presence of HMPA, but not 12C4; (ii) metathesis of **1** with sodium- or potassium-*tert*-butoxide does not generate fully deprotonated complexes (even with excess *n*-butyllithium and the heavier alkali metal alkoxide present, which will be superbasic in nature, as noted below), but the same metathesis reactions with 2-phenylaminopyridine carried out in the presence of 15C5 or 18-crown-6 (18C6) yield fully metallated sodium and potassium complexes [20]; (iii) methylsodium and potassium hydride afford the corresponding fully metallated complexes in the presence of 12C4 [20]; (iv) refluxing in toluene or THF consistently gave **1**, even with a large (ca fivefold) excess of *n*-butyllithium, and the use of methyl- or *tert*-butyllithium instead did not affect the outcome of the reaction. Thus, it would appear that deprotonation of 2-phenylaminopyridine is dependent upon the presence of a suitable Lewis base, e.g., HMPA, 15C5, 18C6, but *not* 12C4, and, in the absence of a suitable Lewis base, a metallation reagent that contains an alkali metal heavier than lithium.

Metathesis of **1** with sodium- or potassium-*tert*-butoxide consistently generates the corresponding sodium and potassium complexes $[\{\mathrm{Na}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)}\cdot\mathrm{HN(Py)(Ph)}\}]$ (**2**) and $[\{\mathrm{K}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)}\cdot\mathrm{HN(Py)(Ph)}\}]$ (**3**), respectively, in excellent yields, even with excess *n*-butyllithium and heavier alkali metal alkoxide present (Eq. (2)). This is surprising, as a mixture of *n*-butyllithium and potassium-*tert*-butoxide is the classic example of a superbase [21], which is a powerful deprotonating agent. The ^{1}H and ^{13}C NMR spectra are consistent with the proposed formulations, the ^{1}H spectra exhibiting a signal attributed to NH at 8.12 and 8.88 ppm, respectively, for the Na and K complexes. Satisfactory microanalyses were obtained for **2** and **3**.

$$[\{\mathrm{Li}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)} \cdot \mathrm{HN(Py)(Ph)}\}] + \mathrm{Bu}^n\mathrm{Li} + 2\mathrm{Bu}^t\mathrm{OM} \rightarrow [\{\mathrm{M}(12\mathrm{C}4)_2\}\{\mathrm{N(Py)(Ph)} \cdot \mathrm{HN(Py)(Ph)}\}] + \mathrm{Bu}^t\mathrm{OLi} + \text{“}\mathrm{Bu}^n\mathrm{Li} \cdot \mathrm{Bu}^t\mathrm{OM}\text{”} \quad (\mathrm{M} = \mathrm{Na\ or\ K}) \qquad (2)$$

The structure of **1**, determined by X-ray crystallography, is shown in Fig. 1 and selected bond lengths can be found in Table 1. The complex crystallises as discrete ion pairs. The lithium cation is sandwiched between two 12-crown-4 molecules in a staggered conformation, to give pseudo-D_{4d} symmetry. The Li–O bond lengths span the range 2.235(4)–2.494(4) Å, within the range reported in the complexes $[\{\mathrm{Li}(12\mathrm{C}4)_2\}\ (\mathrm{SMes}^*)]$ ($\mathrm{Mes}^* = 2,4,6\text{-}\mathrm{Bu}^t{}_3\mathrm{C}_6\mathrm{H}_2$) [22], $[\{\mathrm{Li}(12\mathrm{C}4)_2\}\ (\mathrm{PPh}_2)]$ [23] and $[\{\mathrm{Li}(12\mathrm{C}4)_2\}\{(\mathrm{Me}_3\mathrm{Si})\mathrm{C}(\mathrm{SiBu}^t_2\mathrm{Me})(\mathrm{SiMe}_2\mathrm{F})\}]$ [24]. This results in the lithium cation being displaced from the oxygen mean plane of each crown by 1.317 and 1.340 Å (the mean plane is fitted to the oxygen atoms of the crown). In **1** the dihedral angle between the two mean planes is 0.5°, so they are essentially parallel. The second crown [O(5)–O(8)] exhibits disorder in the ethylene bridges, with common oxygen positions in both components. The composite anion comprises an amide (de-

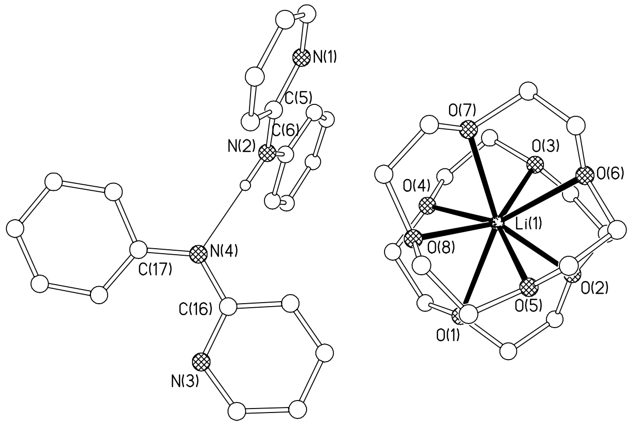

Fig. 1. The cation and anion of **1**, without carbon-bound H atoms and second disorder components. Selected atoms are labelled.

protonated amine), hydrogen bonded to a molecule of the parent secondary amine, both of them with a *Z* configuration [25]. The amine centre is essentially planar (sum of angles 359.9°), indicating sp^2 hybridisation of N. The amine molecule is disordered over two orientations, with exchange of the phenyl and pyridyl rings, since the pyridyl N atom is not involved in any intermolecular interactions that would generate a preference for one site (there is a weak C–H...N intramolecular hydrogen bond between the phenyl and pyridyl groups). This renders the observed bond lengths within the rings somewhat unreliable, as they are averages of two inequivalent sets, but they are in the range observed in a crystallographic study of the parent secondary amine [25]. The amine molecule is close to planar, with a dihedral angle of only 1.6° between the two aromatic rings. The amine forms a hydrogen bond to the amido N centre of the accompanying amide anion, with refined N–H = 0.93(3) Å, N...H = 1.94(3) Å, and an N–H...N angle of 178(2)°. Like the amine molecule, the amide anion is disordered over two orientations, with exchange of the phenyl and pyridyl rings. The anion deviates from planarity more than does the amine, the dihedral angle between the two aromatic rings being 18.2°. This is a consequence of greater steric interaction between the two rings in the amide, the C–N–C angle at the amide N atom being 124.37(18)°, while that at the amine N atom is 131.11(19)°; this difference is as expected when an electron lone pair is compared with an N–H bond. The mean planes of the amine and amide portions of the composite hydrogen-bonded anion have a dihedral angle of 79.7°, so they are approximately perpendicular to each other, rotated about the hydrogen bond out of coplanarity.

The structure of compound **2** is shown in Fig. 2 and selected bond lengths can be found in Table 1. The complex crystallises as discrete ion pairs, crystallographically isomorphous and isostructural with **1**. The sodium cation is sandwiched between two 12-crown-4 molecules in a staggered conformation with pseudo-D_{4d} symmetry. The Na–O bond lengths span the range 2.4224(16)–2.5262(16) Å, longer than the Li–O bond lengths in **1**, in accord with the larger ionic radius of sodium. This range is consistent with those reported in the complexes [{Na(12C4)$_2$}(ClO$_4$)] [26], [{Na(12C)$_2$}(UCl$_4$O$_2$)] [27] and [{Na(12C4)$_2$}{Yb[N(SiMe$_3$)$_2$]$_3$ OSi Me$_3$}] [28]. This results in the sodium cation being displaced 1.452 and 1.458 Å from the mean planes of the two crown ligands and reflects the poorer fit than that of lithium with 12-crown-4. The dihedral angle between the two mean planes of this sandwich is 0.6°. The second crown [O(5)–O(8)] exhibits disorder of the ethylene bridges over two positions with common oxygen positions in both components. The composite anion comprises a deprotonated amide, hydrogen-bonded to a molecule of parent amine. The amine centre is, again, planar [sum of angles 360.0°]. Disorder of phenyl and pyridyl rings is observed. The amine molecule is close to planar, with a dihedral angle between the two aromatic rings of only 0.6°. The hydrogen bond geometry is essentially the same as in **1**, with N–H = 1.03(2) Å, H...N = 1.86(2) Å, and N–H...N = 176(2)°. The amide anion has a dihedral angle of 19.0° between the two aromatic rings, and the amine and amide parts of the composite anion have a dihedral angle of 80.4°. The C–N–C angles are 130.70(19)° in the amine and 124.00(17)° in the amide.

Complex **3** crystallises as discrete ion pairs similar to **1** and **2**. However, there are three pairs in the asymmetric unit of this crystal structure (together with one benzene solvent molecule), which are essentially identical in terms of bond lengths; one pair is shown in Fig. 3 and selected bond lengths can be found in Table 1. Each potassium cation is sandwiched between two 12-crown-4 molecules in a staggered conformation with pseudo-D_{4d} symmetry, similar to Li in **1** and Na in **2**. The larger ionic radius of potassium is reflected in the larger values of the K–O bond lengths which span the range 2.689(5)–2.839(6) Å. This range is in good agreement with those reported in the complexes [{K(12C4)$_2$}{SnCl$_2$[Cr(CO)$_5$]$_2$}] [29] and [{K(12C4)$_2$}Na] [30]. The displacements of the potassium cations from the mean planes of their crown ligands are in the range 1.876–1.924 Å, reflecting the poorer host–guest fit compared with lithium and sodium. The effect of the larger and softer potassium centre can be seen in the dihedral angle between the two crown mean planes, which lies between 12.9° and 19.5°. This bending partially opens up one coordination site, which in solution may allow multihapto interactions; this may be an explanation for the solubility of **3** in arene solvents in contrast to **2**, which displays very low solubility in arene solvents. The composite anion is structurally essentially the same as for **1** and **2.** The amine centres are essentially planar

Table 1
Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**

1			
Bond lengths			
Li(1)–O(1)	2.494(4)	Li(1)–O(2)	2.360(4)
Li(1)–O(3)	2.317(4)	Li(1)–O(4)	2.235(4)
Li(1)–O(5)	2.281(4)	Li(1)–O(6)	2.466(4)
Li(1)–O(7)	2.347(4)	Li(1)–O(8)	2.332(4)
N(2)–C(5)	1.374(3)	N(2)–C(6)	1.379(3)
N(4)–C(16)	1.366(3)	N(4)–C(17)	1.366(3)
Bond angles			
C(5)–N(2)–C(6)	131.11(19)	C(16)–N(4)–C(17)	124.37(18)
2			
Bond lengths			
Na(1)–O(1)	2.5261(16)	Na(1)–O(2)	2.4600(16)
Na(1)–O(3)	2.4340(16)	Na(1)–O(4)	2.4249(16)
Na(1)–O(5)	2.4224(16)	Na(1)–O(6)	2.5006(18)
Na(1)–O(7)	2.4714(18)	Na(1)–O(8)	2.4396(17)
N(2)–C(5)	1.369(3)	N(2)–C(6)	1.380(3)
N(4)–C(16)	1.364(3)	N(4)–C(17)	1.377(3)
Bond angles			
C(5)–N(2)–C(6)	130.70(19)	C(16)–N(4)–C(17)	124.00(17)
3			
Bond lengths			
K(1)–O(1)	2.711(6)	K(1)–O(2)	2.837(6)
K(1)–O(3)	2.839(6)	K(1)–O(4)	2.818(6)
K(1)–O(5)	2.790(5)	K(1)–O(6)	2.782(4)
K(1)–O(7)	2.714(4)	K(1)–O(8)	2.781(4)
K(2)–O(9)	2.737(6)	K(2)–O(10)	2.770(4)
K(2)–O(11)	2.765(5)	K(2)–O(12)	2.709(5)
K(2)–O(13)	2.750(5)	K(2)–O(14)	2.746(4)
K(2)–O(15)	2.742(4)	K(2)–O(16)	2.757(4)
K(3)–O(17)	2.689(5)	K(3)–O(18)	2.793(4)
K(3)–O(19)	2.820(6)	K(3)–O(20)	2.746(6)
K(3)–O(21)	2.726(4)	K(3)–O(22)	2.717(4)
K(3)–O(23)	2.734(5)	K(3)–O(24)	2.816(5)
N(2)–C(5)	1.383(7)	N(2)–C(6)	1.388(7)
N(4)–C(16)	1.347(6)	N(4)–C(17)	1.391(6)
N(6)–C(27)	1.376(7)	N(6)–C(28)	1.380(7)
N(8)–C(38)	1.365(6)	N(8)–C(39)	1.378(6)
N(10)–C(49)	1.386(7)	N(10)–C(50)	1.373(7)
N(12)–C(60)	1.343(6)	N(12)–C(61)	1.383(5)
Bond angles			
C(5)–N(2)–C(6)	131.1(5)	C(16)–N(4)–C(17)	124.9(4)
C(27)–N(6)–C(28)	130.6(5)	C(38)–N(8)–C(39)	124.3(4)
C(49)–N(10)–C(50)	130.6(5)	C(60)–N(12)–C(61)	125.4(4)

(sum of angles 359.7°–360.0°). The observed bond lengths are in agreement with those observed in **1** and **2**. The three amines deviate somewhat more from planarity, with dihedral angles of 2.6°, 11.4° and 15.0° between the two aromatic rings, while the corresponding angles for the amides are 17.4°, 14.7° and 12.3°. The dihedral angles between amine and amide components are 86.9°, 88.0° and 87.2°. C–N–C angles are 130.6(5)°–131.1(5)° for the amine N atoms, and 124.3(4)°–125.4(4)° for the amides. The hydrogen bonds have N–H distances of 0.83(5)–0.92(6) Å, H...N distances of 1.93(6)–2.11(5) Å, and angles of 168(4)°–171(5)° at H.

It is interesting to note that, in all three complexes reported here, the same structural motif of a discrete ion pair is adopted, the alkali metal cation being encapsulated between two crown ether ligands and the amide anion being hydrogen bonded to a molecule of its parent amine. This is in marked contrast to the 2-trimethylsilylaminopyridine derivatives, which exhibited a distinct tendency to adopt structures in which the amide acts as a ligand to the alkali metal [7,9]. Clearly, the substitution of a trimethylsilyl group by a phenyl ring has a marked impact upon the properties of the amide ligand in steric and electronic terms. Sterically, depro-

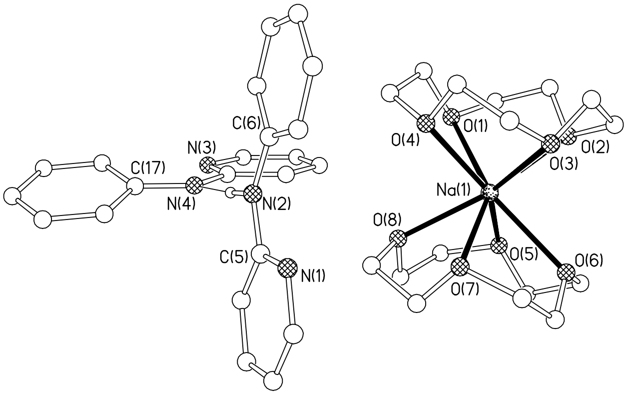

Fig. 2. The cation and anion of **2**, without carbon-bound H atoms and second disorder components. Selected atoms are labelled. The view direction is different from that for Fig. 1.

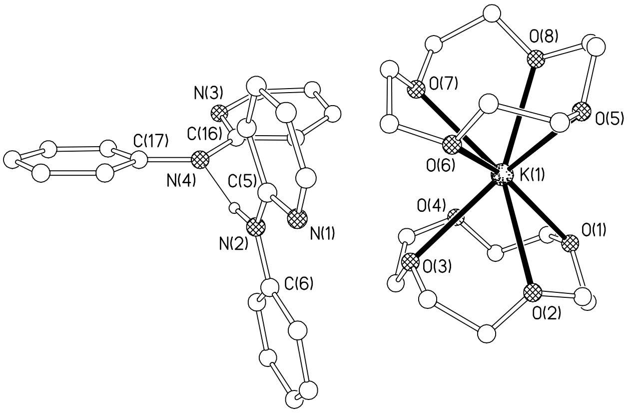

Fig. 3. One cation and one anion of **3**, without carbon-bound H atoms and second disorder components. Selected atoms are labelled.

tonation of the parent amine is not as facile as for the silyl variant. Although this may seem odd, given that a trimethylsilyl group is more sterically demanding than a phenyl ring, the trimethylsilyl group lies further away, so its steric bulk is less effective at shielding the amine. Electronically, whereas we have not observed the 2-trimethylsilylamidopyridine ligand as a free anion, the 2-phenylamidopyridine anion is readily isolated as the free anion; this indicates a greater stabilisation of charge by delocalisation into the two substituent aromatic rings.

We note finally that a structurally homologous series of Li, Na and K complexes with the same ligands and counter-ions is unusual, the variation in size and hardness of the metal cations generally leading to changes of structure.

3. Conclusion

Three new alkali metal complexes containing discrete ion pairs have been synthesised as a consequence of the difficulty of deprotonating the secondary amine 2-phenylaminopyridine in the absence of suitable Lewis base donor molecules. This results in complexes where secondary amine is present, which is not deprotonated by available lithium alkyl. The preference for discrete ion pairs over neutral complex molecules indicates the impact of the substitution of a trimethylsilyl group by a phenyl group, resulting in an amide anion that readily exists as the uncoordinated anion.

4. Experimental

4.1. General comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ethereal, aromatic, and aliphatic solvents were distilled from sodium-benzophenone ketyl radical under an atmosphere of dry nitrogen and were stored over activated 4A sieves. 12-Crown-4 was dried by and stored over activated 4A sieves. Butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes and was used as supplied. Sodium- and potassium-*tert*-butoxide were purchased from Aldrich and baked at 100 °C for 4 h (10^{-2} Torr) prior to use. Deuteriated THF was distilled from a potassium mirror, deoxygenated by three freeze–pump–thaw cycles, and stored over activated 4A sieves.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer operating at 200.1 and 50.3 MHz respectively and chemical shifts are quoted in ppm relative to tetramethylsilane. Elemental analyses were obtained by Elemental Microanalysis Ltd., Okehampton, UK.

4.2. Preparation of $[\{Li(12C4)_2\}\{N(Py)(Ph)\cdot HN(Py)(Ph)\}]$ *(**1**)*

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 12-crown-4 (0.32 mL, 2.00 mmol) and toluene (10 mL). Dropwise addition of $Bu^{n}Li$ (0.8 mL, 2.00 mmol) afforded a yellow solution. On standing for four days the solution turned red and deposited a crop of yellow hexagonal crystals. The mother liquor was removed and the crystals washed with petrol (3 × 5 mL). Recrystallisation of these crystals from THF at −20 °C gave crystals of **1** suitable for an X-ray study (0.52 g, 74.4%). Microanalysis for (**1**): C, 68.07; H, 7.48; N, 6.81%. $C_{38}H_{51}N_4O_8Li\cdot C_6H_5CH_3$ requires C, 68.34; H, 7.52; N, 7.08%. Spectroscopic data for **1**: δ_H ($[^{2}H]_8$ THF) 3.69 (32 H, s, 12C4), 6.32 (2 H, t, β-H–Py), 6.75 (2 H, t, γ-H–Py), 6.79 (2 H, d, β′-H–Py), 7.17 (4 H, d, *ortho*-H–Ph), 7.22 (2 H, t, *para*-H–Ph), 7.32 (4 H,t, *meta*-H–Ph), 7.94 (2 H, d, α-H–Py) and 8.22 (1 H, s, N–H). δ_C ($[^{2}H]_8$ THF) 73.14 (12C4), 106.77 (β-C–Py), 111.33 (γ-C–Py), 116.91 (β′-C–Py), 124.10 (*ortho*-C–Ph), 130.86 (*para*-C–Ph), 137.22 (*ipso*-C–Ph), 151.78 (*meta*-C–Ph), 159.83 (α-C–Py) and 169.13 (α′-C–Py). δ_{Li} ([^{2}H]$_8$ THF) 1.35 (s).

*4.3. Preparation of [{Na(12C4)$_2$}{N(Py)(Ph)·HN(Py)(Ph)}] (**2**)*

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 12-crown-4 (0.32 mL, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}ONa (0.19 g, 2.00 mmol) with gentle heating gave an orange solution, which deposited a yellow precipitate on cooling. Removal of volatiles in vacuo and recrystallisation from hot THF gave crystals of **2** suitable for an X-ray study (0.68 g, 95.1%). Microanalysis for **2**: C, 62.78; H, 7.50; N, 7.03%. $C_{38}H_{51}N_4O_8Na$ requires C, 63.85; H, 7.19; N, 7.84%. Spectroscopic data for **2**: δ_{H} ([^{2}H]$_8$ THF) 3.68 (32 H, s, 12C4), 6.54 (2 H, t, β-H–Py), 6.78 (2 H, d, β′-H–Py), 6.83 (2 H, t, γ-H–Py), 7.25 (4 H, t, *meta*-H–Ph), 7.39 (2 H, t, *para*-H–Ph), 7.32 (4 H, d, *ortho*-H–Ph), 7.95 (2 H, d, α-H–Py) and 8.12 (1 H, s, N–H). δ_{C} ([^{2}H]$_8$ THF) 73.84 (12C4), 112.46 (β-C–Py), 115.19 (β′-C–Py), 122.56 (γ-C–Py), 122.79 (*meta*-C–Ph), 131.79 (*para*-C–Ph), 139.76 (*ipso*-C–Ph), 148.88 (*ortho*-C–Ph), 151.37 (α-C–Py) and 162.28 (α′-C–Py).

*4.4. Preparation of [{K(12C4)$_2$}{N(Py)(Ph)·HN(Py)(Ph)}]·1/3C$_6$H$_6$ (**3**)*

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 12-crown-4 (0.32 mL, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}OK (0.22 g, 2.00 mmol) with gentle heating gave an orange solution, which deposited a yellow precipitate on cooling. Removal of volatiles in vacuo and recrystallisation from hot benzene gave crystals of **3** suitable for an X-ray study (0.55 g, 75.2%). Microanalysis for **3**: C, 58.71; H, 7.57; N, 5.26%. $C_{38}H_{51}N_4O_8K$ requires C, 59.9; H, 7.06; N, 6.96%. Spectroscopic data for **3**: δ_{H} ([^{2}H]$_8$ THF) 3.59 (32 H, s, 12C4), 6.16 (2 H, t, β-H–Py), 6.58 (2 H, t, γ-H–Py), 6.73 (2 H, d, β′-H–Py), 7.05 (2 H, t, *para*-H–Ph), 7.09 (4 H, t, *meta*-H–Ph), 7.28 (4 H, d, *ortho*-H–Ph), 7.93 (2 H, d, α-H–Py) and 8.88 (1 H, s, N–H). δ_{C} ([^{2}H]$_8$ THF) 73.84 (12C4), 112.46 (β-C–Py), 115.19 (γ-C–Py), 122.56 (β′-C–Py), 122.79 (*para*-C–Ph), 131.79 (*meta*-C–Ph), 139.76 (*ipso*-C–Ph), 148.88 (*ortho*-C–Ph), 151.37 (α-C–Py) and 162.28 (α′-C–Py).

4.5. X-ray crystallography

Crystal data for complexes **1**, **2**, and **3** are listed in Table 2. Crystals were examined on a Bruker AXS

Table 2

Compound	**1**	**2**	**3**
Formula	$C_{38}H_{51}LiN_4O_8$	$C_{38}H_{51}N_4NaO_8$	$C_{38}H_{51}KN_4O_8 \cdot 1/3C_6H_6$
Formula weight	698.8	714.8	757.0
Temperature (K)	160	160	160
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions			
a (Å)	11.7157(13)	11.9759(7)	13.1117(6)
b (Å)	24.420(3)	24.4278(15)	24.5590(10)
c (Å)	13.0172(14)	13.0445(8)	37.7496(16)
β (°)	103.667(11)	102.796(2)	
V (Å^3)	3618.7(7)	3721.3(4)	12155.8(9)
Z	4	4	12
Absorption coefficient (mm^{-1})	0.089	0.099	0.186
Crystal size (mm)	0.42 × 0.32 × 0.30	0.66 × 0.22 × 0.16	0.80 × 0.72 × 0.68
$\theta_{\max}$ (°)	25.0	25.0	25.0
Reflections measured	18 905	22 382	29 605
Unique reflections	6321	6541	20 439
Reflections with $F^2 > 2\sigma(F^2)$	3571	3847	12 057
Transmission factors	0.963–0.974	0.937–0.984	0.866–0.884
R_{int}	0.0514	0.0526	0.0285
Number of parameters	540	540	1524
$R^{a}[F^2 > 2\sigma(F^2)]$	0.0471	0.0442	0.0676
R_w^{b} (all data)	0.1249	0.1121	0.1945
Goodness-of-fit^{c}(S)	0.935	0.954	0.980
Largest difference peak and hole (e Å^{-3})	0.30 and −0.21	0.28 and −0.25	0.58 and −0.41

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for 'observed' reflections having $F^2 > 2\sigma(F^2)$.

[b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum_w(F_o^2)^2]^{1/2}$ for all data.

[c] $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. of unique reflections} - \text{no. of parameters})]^{1/2}$.

SMART CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.70173$ Å at 160 K (Oxford Cryostream low temperature device). Cell parameters were refined from positions of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and constrained with a riding model; U(H) was set at 1.2 times U_{eq} for the parent atom. The structure of compound **3** was refined as a racemic twin, with component contributions of 0.74:0.26(5) [31]. Disorder was resolved and refined for the ethylene linker groups in one crown ether ligand in each structure, and for exchange of phenyl and pyridyl rings in every amine and amide; highly anisotropic atomic displacement parameters indicate the possibility of further, unresolved disorder in other crown ether linkages in compound **3**. Programs were Bruker AXS SMART (control) and SAINT integration [32], and SHELXTL for structure solution, refinement and molecular graphics [33].

5. Supplementary information

Crystallographic data for the structural analysis of **1**, **2**, and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 212542, 212543, and 212544 for compounds **1**, **2**, and **3** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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